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A REVISION OF THE ATOMIC WEIGHT OF LEAD: THE ANALYSIS OF LEAD BROMIDE AND CHLORIDE

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Presented to the Academy, January 3, 1914

In a recent paper by Baxter and Wilson¹ the atomic weight of lead was found from analyses of fused lead chloride, by comparison with pure silver and by weighing the silver chloride produced. The result of this investigation, $Pb = 207.09$ ($Ag = 107.880$), is considerably higher than most earlier determinations. For this reason and because the work of Baxter and Wilson was essentially preliminary in its nature it was obviously desirable to test the matter further, and ever since the publication of the above paper the atomic weight of lead has been under almost continuous investigation in the Harvard Laboratory. Because of the advantages offered by the greater insolubility of silver bromide, the analysis of lead bromide was next undertaken; and later lead chloride was investigated anew. The outcome of all the work is that the atomic weight of lead is very close to 207.20, a value even higher than that previously found by Baxter and Wilson.

The method of experimentation was the usual one employed with metallic halides. Carefully purified lead bromide, which had been crystallized from concentrated hydrobromic acid solution, was dried by fusion in an atmosphere containing a large proportion of hydrobromic acid gas. The acid was synthesized from hydrogen and bromine, and during a fusion was mixed with either nitrogen, hydrogen, or bromine. After being weighed the salt was dissolved in hot water containing a very small amount of nitric acid, and at low concentration the solution was precipitated with a very dilute solution of a carefully weighed, very nearly equivalent quantity of pure silver. The solution was allowed to stand for some days with occasional shaking, and then was tested in a nephelometer for excess of silver or bromide. If a deficiency of either was found, this deficiency was made up with very dilute standard silver or bromide solution. Then the solution was again tested, and the operations were repeated if necessary. As soon as the exact end-point had been found, a moderate excess of silver nitrate was added, and eventually the silver bromide was collected and weighed. The usual correction for moisture retained by the dried silver bromide was determined and applied.

In order to test the purity of the lead salt, metallic electrodes were prepared from the purified material, and the ultraviolet spark spectrum of the metal was photographed by means of a Féry quartz spectrograph. The only lines which could be detected were those commonly ascribed to lead. In fact the original material was fairly pure, containing only traces of silver, copper, and iron, which rapidly disappeared in the course of the purification. Incidentally we found that 0.004% of copper in lead yields fairly strong copper lines and that 0.0001% of silver could readily be detected. Our material was further tested in a sensitive gold leaf electroscope, but showed no evidence of radioactivity.

Several difficulties were met which deserve special attention. Lead bromide, when dissolved in water, hydrolyses to give an insoluble basic bromide. This phenomenon was first met with material which had been fused in an atmosphere containing a large proportion of hydrobromic acid gas, but it was also found that even unfused salt which has been crystallized from concentrated hydrobromic acid solution, and which probably contains a small amount of the latter substance, hydrolyses in the same way, and, apparently to about the same extent. Thus it was evident that at any rate the greater part of the hydrolysis occurred during the solution of the salt and not during the fusion. The evidence that *no* hydrolysis with loss of bromine occurred during the fusion is that the different samples of fused salt, in spite of the widely varied atmospheres in which they were fused, were essentially identical in composition, and that the atomic weight of lead found from the bromide agrees very closely with that found later in this research by analysis of the chloride.

In order to prevent the basic salt from forming during the solution of the bromide, a small quantity of nitric acid was added to the hot water in which the salt was dissolved. It was proved experimentally that the nitric acid added was far too small in amount to cause loss of either bromine or hydrobromic acid from the solution.

A second difficulty was caused by the presence of a small amount of black insoluble material in the fused salt. Although puzzling at first, this was eventually found to consist partly of carbon, partly of silica. The greatest care in the purification of the material failed to eliminate the trouble entirely, although the proportion of insoluble residue was reduced on an average to 0.004%. Error from this source was avoided by filtering the lead bromide solution through a weighed platinum-sponge crucible in each analysis before precipitation of the silver bromide, and weighing the residue.

The weights given in the tables are converted to the vacuum standard by applying the following corrections for each apparent gram of substance: PbBr_2 , +0.000036; PbCl_2 , +0.000060, Ag, -0.000031; AgBr , +0.000041; AgCl , +0.000071.

The analyses in the following table were made by F. L. Grover. Two preliminary series, one by T. Thorvaldson and one by Grover, gave essentially the same result, but since the insoluble residue was not determined in these experiments, the details are not given.

THE ATOMIC WEIGHT OF LEAD
 $\text{PbBr}_2 : 2\text{Ag} : 2\text{AgBr}$
 Ag = 107.880 Br = 79.916

FUSION ATMOSPHERE	GRAMS OF PbBr_2	GRAMS OF Ag	RATIO $\text{PbBr}_2 : 2\text{Ag}$	ATOMIC WEIGHT OF Pb	GRAMS OF AgBr	RATIO $\text{PbBr}_2 : 2\text{AgBr}$	ATOMIC WEIGHT OF Pb
HBr+ H_2	5.27845	3.10271	1.70124	207.23			
HBr+ H_2	2.65094	1.55822	1.70126	207.23			
HBr+ N_2	4.08410	2.40104	1.70097	207.17			
HBr+ N_2	4.97468	2.92473	1.70090	207.15			
HBr+ N_2	4.05541	2.38398	1.70111	207.20	4.15017	0.97717	207.18
HBr+ N_2	3.44139	2.02288	1.70123	207.23	3.52224	0.97705	207.14
HBr+ N_2	5.17387	3.04158	1.70105	207.19	5.29498	0.97713	207.17
HBr+ N_2	3.84497	2.26022	1.70115	207.21	3.93446	0.97726	207.22
HBr+ H_2	4.30513	2.53086	1.70105	207.19	4.40616	0.97707	207.15
HBr+ H_2	4.53445	2.66549	1.70117	207.21	4.64048	0.97715	207.18
HBr+ N_2	5.78437	3.40044	1.70107	207.19	5.91976	0.97713	207.17
HBr+ N_2	4.87079	2.86337	1.70107	207.19	4.98467	0.97715	207.18
HBr+ N_2	6.28446	3.69447	1.70104	207.19	6.43124	0.97718	207.19
HBr+ N_2	4.74639	2.79011	1.70115	207.21	4.85708	0.97721	207.20
HBr+ N_2	6.82424	4.01148	1.70118	207.21	6.98380	0.97715	207.18
HBr+ N_2	6.53689	3.84274	1.70110	207.20			
HBr+ Br_2	4.10098	2.41088	1.70103	207.18	4.19791	0.97691 ¹	207.09 ¹
HBr+ Br_2	2.64256	1.55352	1.70101	207.18			
HBr+ Br_2	6.30683	3.70718	1.70125	207.23			
		Average	1.70111	207.20		0.97715	207.18

¹ This result is omitted in computing the average.

Since the result of these analyses of lead bromide is even higher than that obtained by Baxter and Wilson, lead chloride also was investigated anew by essentially the same method as was used in the work with the bromide. The chloride was finally dried by fusion in a current of hydrochloric acid gas.

In preliminary experiments to our surprise a basic salt precipitated during the solution of the lead chloride in hot water, as soon as a very considerable proportion of the salt was dissolved, although a similar phenomenon was never observed in the earlier research upon the chloride.

One marked difference, however, exists between the two cases. In the experiments by Baxter and Wilson from 4 to 5 grams of salt were dissolved in a liter of water, whereas in our first experiments 8 to 9 grams of salt were dissolved in the same volume. In other words the basic salt precipitates only at high concentrations

As in the case of the bromide, uncertainty exists as to whether the basic salt is formed during the fusion of the slightly damp material, even in the presence of a high hydrochloric acid concentration, or whether it is due to hydrolysis during solution. Since, however, we found that lead chloride which has been crystallized from dilute hydrochloric acid solution, when dissolved in enough hot water to yield a solution nearly saturated at room temperature (about 10 g. per liter), yields a similar insoluble compound which dissolves readily in dilute acid and contains chlorine, the latter explanation seems the more probable one.

More direct evidence that the fused chloride is neutral was obtained as follows: Chloride which had been crystallized from very dilute hydrochloric acid solution was dried in a vacuum at room temperature. Weighed portions were then fused in a current of hydrochloric acid gas and the loss in weight due to water was found. The fused portions were compared with silver in the usual way, and at the same time other weighed portions of the vacuum-dried material were similarly analyzed. After correction for the moisture retained by the unfused material, both fused and unfused salt were found to possess the same composition.

Further evidence that the fused salt is free from basic chloride, is afforded by the agreement of the chloride analyses among themselves, as well as with the results of the bromide analyses.

In dissolving the fused salt for analysis the precipitation of the basic salt was prevented as with the bromide by adding a small amount of nitric acid to the hot water in which the chloride was dissolved. It was proved experimentally that no chlorine is lost in this way.

Furthermore, as with the bromide, the fused chloride usually contained a trace of black insoluble matter, in spite of the utmost care in the purification of the salt and in the preparation of the hydrochloric acid gas in which the salt was fused. Since, however, this residue was collected upon a weighed platinum-sponge crucible, and since, after it had been weighed, a correction was applied, no appreciable error from this source could have occurred. The average per cent of the black residue found in the chloride was essentially the same as that found in the bromide.

The source of the lead material used in the preparation of the lead bromide and a portion of the lead chloride is unknown to us. Both commercial metal and commercial lead nitrate were employed. Be-

cause the atomic weight of radioactive lead has recently been found to differ from that of ordinary lead² we also undertook the examination of inactive lead from widely different geographical sources. Lead nitrate was prepared from the various minerals, and after crystallization was converted to lead chloride. The latter in turn was several times crystallized from dilute hydrochloric acid solution, fused and analyzed by comparison with silver. Each specimen of lead nitrate was carefully examined spectroscopically as previously described, and not the slightest difference could be detected between the different specimens. Furthermore the radioactivity of all the minerals was tested in a sensitive gold-leaf electroscope and no one of them was found to increase the normal leak of the instrument by a measurable amount.

In the experiments with lead chloride no attempt was made to collect the silver chloride obtained in the comparisons with silver. Instead, in separate experiments with new portions of the chloride, silver chloride was precipitated with an excess of silver nitrate and the precipitate was collected and weighed.

The analyses in the following table were made by Grover.

THE ATOMIC WEIGHT OF LEAD

$\text{PbCl}_2 : 2\text{Ag}$ $\text{PbCl}_2 : 2\text{AgCl}$
 $\text{Ag} = 107.880$ $\text{Cl} = 35.457$

SOURCE OF MATERIAL	GRAMS OF PbCl_2	GRAMS OF Ag	RATIO $\text{PbCl}_2 : 2\text{Ag}$	ATOMIC WEIGHT OF Pb	GRAMS OF AgCl	RATIO $\text{PbCl}_2 : 2\text{AgCl}$	ATOMIC WEIGHT OF Pb
Commercial Nitrate	5.63567	4.37200	1.28904	207.21			
	5.58730	4.33427	1.28910	207.22			
	6.86319	5.32402	1.28910	207.22			
Average.....			1.28908	207.22			
Joplin, Mo, U. S. A. ¹	4.70770	3.65223	1.28899	207.20			
	4.20222	3.25968	1.28915	207.23			
Average			1.28907	207.22			
Wallace, Id. U. S. A. ²	7.04688	5.46691	1.28901	207.20			
	5.88935	4.56868	1.28907	207.22			
Average			1.28904	207.21			
Wallace, Id. U. S. A. ²	6.96370				7.17754	0.97021	207.22
	6.89046				7.10231	0.97017	207.21
Average						0.97019	207.21
Tucson, Ariz., U. S. A. ³	4.90083	3.80171	1.28911	207.22			
	5.79300	4.49404	1.28904	207.21			

¹ Galena; ² Cerussite; ³ Vanadinite and Wulfenite.

THE ATOMIC WEIGHT OF LEAD—Continued

SOURCE OF MATERIAL	GRAMS OF PbCl ₂	GRAMS OF Ag	RATIO PbCl ₂ :2Ag	ATOMIC WEIGHT OF Pb	GRAMS OF AgCl	RATIO PbCl ₂ : 2AgCl	ATOMIC WEIGHT OF Pb
Average			1.28908	207.22			
Metalline Falls, Wash, U. S. A. ¹	5.43965 5.74504	4.21992 4.45674	1.28908 1.28907	207.21 207.22			
Average			1.28906	207.21			
Nassau, Germany ¹	6.57216 5.66330	5.09849 4.39340	1.28904 1.28905	207.21 207.21			
Average			1.28905	207.21			
Eifel Mts., Germany ²	5.73434 4.17445	4.44857 3.23862	1.28903 1.28896	207.21 207.19			
Average			1.28900	207.20			
New South Wales ²	6.25884 5.25882	4.85584 4.07933	1.28893 1.28914	207.19 207.23			
Average			1.28904	207.21			
New South Wales ²	7.33227 6.51699				7.55732 6.71690	0.97022 0.97024	207.22 207.23
Average						0.97023	207.23
Average of all experiments			1.28905	207.21		0.97021	207.22

¹ Galena; ² Cerussite.

SUMMARY OF ATOMIC WEIGHT VALUES

PbBr ₂ :2Ag.....	207.20
PbBr ₂ :2AgBr.....	207.18
PbCl ₂ :Ag.....	207.21
PbCl ₂ :2AgCl.....	207.22
Average.....	207.20

The close agreement of the chloride analyses with those of the bromide is very reassuring; for it is difficult to believe that any constant error, such as hydrolysis of the salts during fusion, could have affected both series of results to the same extent. Furthermore it is obvious that the different specimens of lead chloride are identical within the limit of experimental error, and that ordinary lead, if composed wholly or in part of isotopes, is astonishingly constant in composition.

The results of this investigation indicate (1) that lead bromide and chloride after fusion in atmospheres containing hydrobromic acid and hydrochloric acid respectively are neutral, (2) that no difference exists

between specimens of lead of different geographical origin, and (3) that the atomic weight of lead referred to silver as 107.880 is very nearly 207.20.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in the pursuit of this investigation.³

¹ *Proc. Amer. Acad.*, **43**, 365 (1907); *J. Amer. Chem. Soc.*, **30**, 187; *Zeit. anorg. Chem.*, **57**, 174.

² See, Richards and Lambert, *J. Amer. Chem. Soc.*, **36**, 1329 (1914); M. Curie, *C. R. Paris Acad. Sci.*, **158**, 1676 (1914); Hönigschmid and St. Horowitz, *Ibid.*, **158**, 1796 (1914); Soddy and Hyman, *J. Amer. Chem. Soc.*, **105**, 1402 (1914).

³ This work will be described in detail before long in *Proc. Amer. Acad. Arts Sci., Boston*, and in *J. Amer. Chem. Soc.*

A REVISION OF THE ATOMIC WEIGHT OF PRASEODYMIUM

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Presented to the Academy, December 16, 1914

Some years ago the atomic weight of neodymium was investigated in the Harvard Chemical Laboratory by the analysis of the chloride;¹ and the success met in obtaining pure material and in the method used, led us to investigate in a similar fashion the atomic weight of the twin element praseodymium. The International Committee upon Atomic Weights has chosen the value 140.6 for this constant, yet some of the recent investigations, notably those of Brauner, have yielded considerably higher results, in the neighborhood of 141.

Naturally, the first problem in the investigation was to prepare pure praseodymium salt. Through the great kindness of Dr. H. S. Miner of the Welsbach Light Company we were fortunate enough to secure as a starting point about 10 kg. of crude praseodymium ammonium nitrate, containing about 50% of the corresponding lanthanum and cerium salts as well as a small amount of neodymium. Since one of the most rapid and effective methods of freeing praseodymium salts from the closely related elements, lanthanum, cerium, neodymium, and samarium is the fractional crystallization of the double ammonium nitrate, we chose this method of purification. In this crystallization the bases separate in the order lanthanum, cerium, praseodymium, neodymium, samarium, and yttrium earths. The usual method of fractional crystallization was followed;² that is, the mother liquor of a less soluble fraction was used for dissolving the crystals of the next more soluble fraction. The crystallization proceeded with the occasional rejection of fairly large fractions, chiefly lanthanum and cerium, at the less soluble end of each series, and the rejection of much smaller fractions, partly neodymium, at the more